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FLAME HEATED THERMIONIC
CONVERTER RESEARCH

Report No. 6
Sixth Quarterly Report
(1 Oct. 1962 to 31 Dec. 1962)
Contract No. DA-36-039 SC-88982

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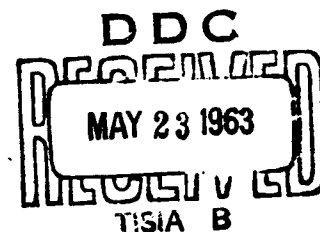
ATOMICS INTERNATIONAL

A DIVISION OF NORTH AMERICAN AVIATION, INC.

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FLAME HEATED THERMIONIC
CONVERTER RESEARCH

Report No. 6
Sixth Quarterly Report
(1 Oct. 1962 to 31 Dec. 1962)

By
W. R. MARTINI
D. H. ADAIR

Object: To develop the technology required for portable
flame-heated thermionic power sources.

ATOMICS INTERNATIONAL

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PURPOSE

The purpose of the procurement is to investigate the various problems encountered in the design and construction of thermionic generators capable of producing from 5 to 200 watts of power. These problems cover:

1) The selection of suitable materials for thermionic diode envelopes and heat ducts where high temperatures and corrosive gases are encountered.

2) The design of a fossil-fuel burner capable of providing the required temperatures and heating rates.

3) The establishment of design parameters for thermionic generators of various power levels from 5 to 200 watts.

4) The construction of a sample generator, rated at 100 watts output, to demonstrate the feasibility of the design approach.

PROGRAM OUTLINE

TASK A - THERMIONIC CONVERTER DEVELOPMENT

1. Development of flame heated converter construction technique
2. Building converters for test

TASK B - HEAT SOURCE DEVELOPMENT

1. Premix burner development
2. Fuel injection burner development
3. Theoretical studies on heat economy and combustion

TASK C - MATERIALS DEVELOPMENT AND EVALUATION

1. Procurement and evaluation of emitter thimble materials and coatings
2. Gas permeation measurements

TASK D - PROTOTYPE DEVELOPMENT

1. Testing flame heated converters
2. Series connection studies
3. Push-pull connection studies
4. System design and construction

TASK E - PROJECT COORDINATION AND REPORTS

Coordinate the various parts of this contract and write seven quarterly technical reports and one final technical report

OTHER PROGRAMS

The following programs at Atomics International are related to the present contract:

1. Company sponsored research on flame heated thermionic converters
2. Office of Naval Research sponsored research on the basic physics of thermionic converters
3. Solar-heated thermionic converters for the Jet Propulsion Laboratory
4. Research on uniform work function diodes for Aeronautical Systems Division, U.S. Air Force

5. Company sponsored research on new emitter and collector materials

6. Company sponsored research on low temperature diode construction methods and on the evaluation of materials for flame corrosion and gas permeation

7. National Aeronautics and Space Administration-sponsored program on nuclear thermionics feasibility demonstration (joint with Thermo Electron Engineering Corporation and Battelle Memorial Institute).

ABSTRACT

TASK A - THERMIONIC CONVERTER DEVELOPMENT

New types of welding techniques have been developed for attaching the coated molybdenum thimble to the converter assembly.

TASK B - HEAT SOURCE DEVELOPMENT

Although satisfactory temperatures and heat fluxes were obtained with burners using premixed air and gas, development was started of burners using fuel injected directly into the combustion chamber. Satisfactory burners employing fuel injection have now been produced.

TASK C - MATERIALS DEVELOPMENT AND EVALUATION

A number of anti-oxidation coatings for molybdenum are now undergoing evaluation, both in the form of coated wires heated electrically and in the form of thimbles heated internally with a flame. One thimble coated internally with TI-Kote was heated for 42 hr at a maximum temperature of 1400°C before failure occurred.

TASK D - PROTOTYPE DEVELOPMENT

Two flame heated converters were tested during this report period. Some power was developed but failure in the coating occurred before any data could be obtained. A model of a multi-diode power source using individually heated diodes is shown.

PUBLICATIONS, LECTURES, REPORTS, CONFERENCES

1. On October 3, 1962, W. R. Martini and R. A. Lockwood attended a briefing and tour at the Thermo Electron Engineering Corporation, Waltham, Massachusetts. The chief item of interest was the gasoline fueled-thermionic diode heater, although other things were also discussed.

2. On October 3, 1962, the above mentioned individuals also attended a meeting at USAELRDL on the subject of gasoline burners and materials. W. R. Martini presented a short discussion on the progress of the contract and representatives of other companies having contracts with the Signal Corps did likewise. Representatives of some companies not having contracts with the Signal Corps talked in a very general way about their work.

3. On October 8, 1962, W. R. Martini visited Mr. Lawrence Sama and Mr. Robert W. Campbell of the General Telephone and Electronics Laboratory, Bayside, New York to talk over their tin-aluminum coating for tantalum and molybdenum.

4. A paper entitled "Design Considerations for Gasoline-Powered Thermionic Generators" by W. R. Martini appeared in the proceedings of the 16th Annual Power Sources Conference sponsored by the Power Sources Division Electronic Components Department, U. S. Army Signal Research and Development Laboratory.

5. An exhibit was prepared for the AUSA Electronics Symposium at Ft. Monmouth, November 13, 1962. It included a model of our proposed power source, the sample product from the first year's work, and posters showing the pertinent information.

TECHNICAL PROGRESS

TASK A - THERMIONIC CONVERTER DEVELOPMENT

Phase 1 - Construction Techniques

Attempts were made to attach diaphram assemblies to a number of different types of coated molybdenum emitter thimbles. Attachment by welding has been the most successful. Some weld beads reduced the minimum internal diameter of the emitter thimble. Now the joint design has been improved so that no internal diameter reduction is obtained. Figure 1 shows a photograph of a test weld of a Kovar outer ring to a molybdenum inner ring. The molybdenum
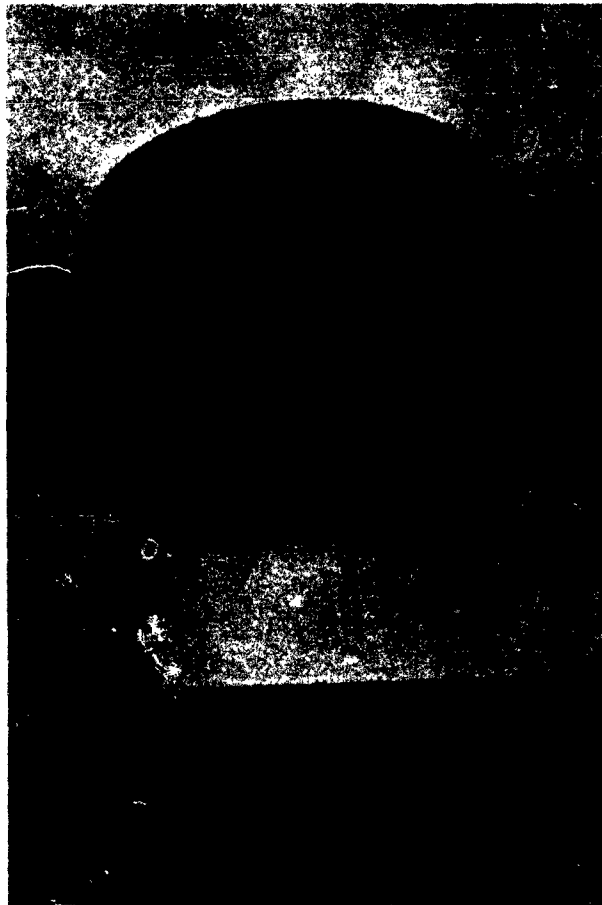
Figure 1. Test Weld - Kovar to Coated Molybdenum

ring had been coated on the inside with tin-aluminum which interfered with the usual welding technique. This joint design can be used when welding directly to the coating is not possible.

Phase 2 - Diode Construction

No diodes have been constructed for flame heating during this quarter. One diode has been constructed on a parallel company-sponsored program in essentially the same way as the flame-heated diodes have been constructed. This diode is to be heated by electron bombardment.

TASK B - HEAT SOURCE DEVELOPMENT

Phase 1 - Premixed Burner Development

During this report period, the vacuum-insulated heating experiment[1] has been reworked to give more and better information. It appeared from early tests that the water flowing through the heat sink did not have time to be thoroughly mixed before it reached the thermocouple measuring the outlet water temperature. Consequently, a new heat sink was made in the form of a hollow copper disk through which the water must pass in a tortuous path. The heat sink has a slot across its diameter as shown in Figure 2 so that the temperature across one entire diameter can be observed with a pyrometer. A water-cooled copper shroud has been added to the vacuum space around the molybdenum thimble. This shroud will pick up most of the heat radiating from the radiation shields around the emitter thimble.

The series of burner tests reported in the last report[1] was continued. Run No. 4 was carried through before the modifications mentioned above were accomplished. The results are shown in Table I. This was the final test using a Durak-B coated molybdenum thimble with a welded end cap and burner hardware as shown in Figure 14 of the Third Quarterly Report.[4] In Table I it is shown that gasoline was run through the burner for part of this test with no apparent difficulty. It is also shown that the temperature of the combustion chamber agrees fairly well with the emitter temperature when: 1) the apparent temperature of the combustion chamber is corrected for the mirror, and 2) the apparent temperature of the emitter is corrected for the mirror, window and emissivity of the molybdenum. The heat flux and heating efficiency results, however, are very disappointing. The molybdenum thimble used in Runs No. 1 to 4 survived 41 hr of heating without failure. Runs No. 6, 7, and 8 were

FUEL

FUEL INJECTOR

SECONDARY AIR

FLUE GAS

PLUG

FLOW DIVIDER

ARM OF PLUG

PRIMARY AIR

RADIATION
SHIELD
COOLING WATER

C.W. OUT

C.W. IN

RADIATION
SHIELDS

GLASS
VACUUM
ENVELOPE

COATED Mo
THIMBLE

COMBUSTION
CHAMBER

HEAT
SINK

JET

OBSERVATION SLOT

C.W. IN

C.W. OUT
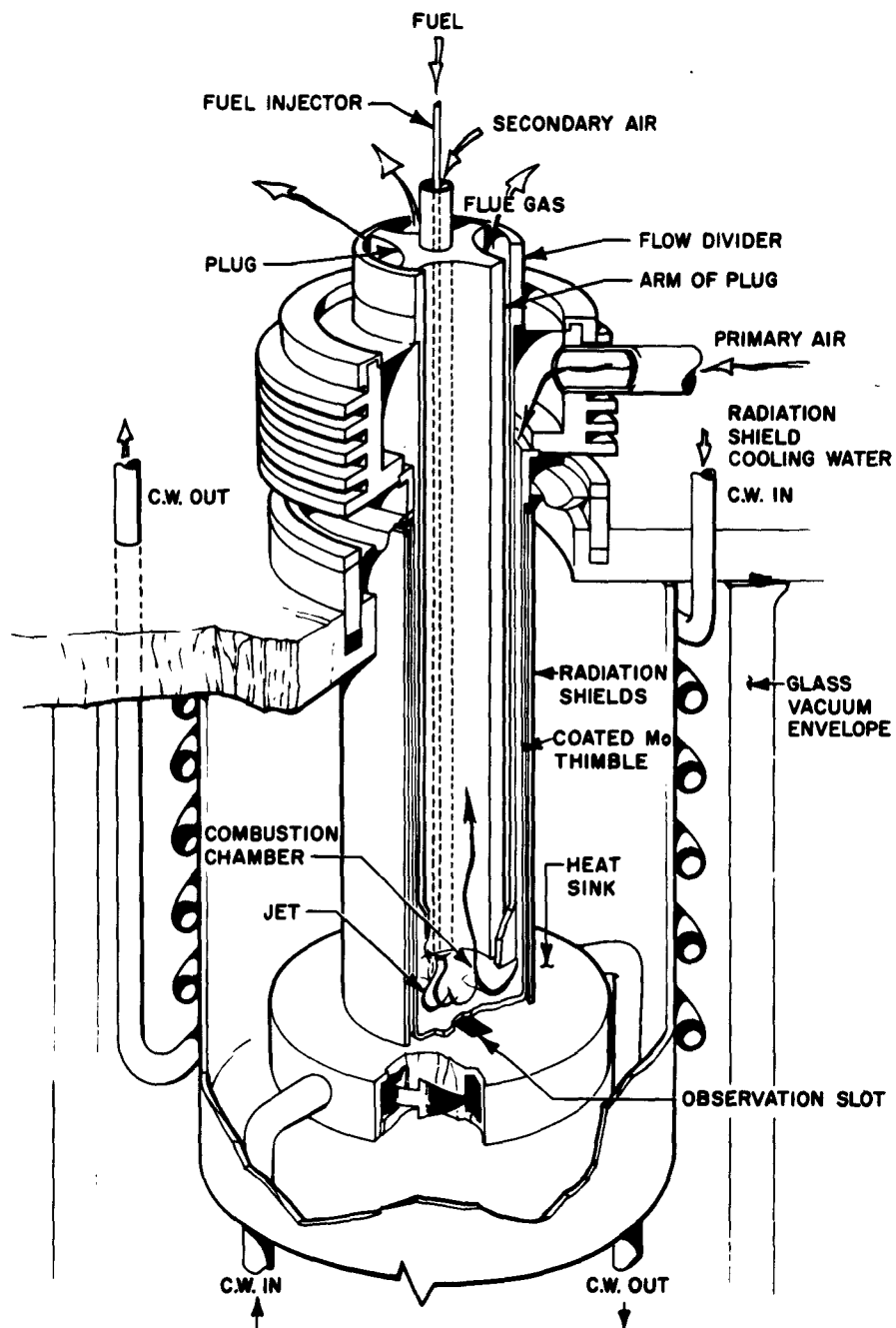
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Figure 2. Vacuum Insulated Burner Experiment

TABLE I

SUMMARY OF VACUUM-INSULATED BURNER EXPERIMENTS

AND FLAME-HEATED DIODE EXPERIMENTS

Run No.	Fuel	Comb. C Temp. (°C)	Emitter Temp. (°C)	Heat Flux (w/cm²)	Heating Eff %	Burner ΔP (in. H₂O)	Duration	Em. Thim.	Burner Type
VB-4a	gasoline	1123	1104	7.5	7.4	0.8	23-1/2 hr 4 cycles	welded Mo	premix
VB-4b	gasoline	1108	1104	4.9	4.8	0.8			
VB-4c	propane	1381	1335	8.8	4.2	3.7			
VB-4d	propane	1393	1345	9.9	4.5	4.5			
VB-6a	propane	--	1072	46	25.5	0.2	7-1/2 hr 3 cycles	Durak-B on deep drawn molybdenum	premix
VB-6b	propane	--	940	48	18.4	0.6			
VB-6c	propane	--	940	48	18.2	0.6			
VB-6d	propane	1140	940	34	19.2	0.6			
VB-7a	propane	1228	1179	24	23.3	0.4			
VB-7b	propane	1249	1179	24	23.6	0.4			
VB-8	propane	1259	1162	20	14.5	1.2			
VB-9a	propane	1058	1038	15	12.6	1.7	3-1/2 hr 3 cycles	Sn-Al on deep drawn molybdenum	fuel injection
VB-9b	propane	1058	1044	29	25	1.7			
VB-9c	propane	1176	1106	24	16.9	1.8			
VB-9d	propane	1068	1049	19	13.4	1.6			
VB-9e	propane	1074	1049	19	9.8	1.9			
VB-9f	propane	1125	1111	17	11.0	2.6			
VB-9g	propane	1130	1128	17	10.8	2.7			
Diode 9	propane	1500	--	--	--	18	2 hr, 1 cycle	Durak-B on deep drawn molybdenum	premix
Diode 10	propane	1550	--	--	--	16	1-1/2 hr, 1 cycle	Durak-B on deep drawn molybdenum	premix

accomplished with one Durak-B coated deep drawn molybdenum thimble. The thimbles survived 7-1/2 hr of heating before a hole ate through the cylindrical wall 0. 1 in. from the inside bottom. Additional description of this thimble failure is given in the discussion of Phase I, Task C. Runs No. 6 to 8 were made with burner hardware made from quartz, which at these temperatures, has a short life due to devitrification. The temperatures are below the region of interest; however, with the new heat sink the heat fluxes are surprisingly high.

The diode heater for diode No. 9 was a premixed burner of advanced design. The combustion chamber was made from KT silicon carbide with posts 1/4 in. high machined out of the top surface. Instead of merely resting on the bottom of the coated molybdenum thimble, however, this combustion chamber was cemented to the bottom of the thimble with silicon carbide cement. The cement contains silicon carbide grain and an oxide binder. The flow divider also was machined from KT silicon carbide to give a 20 mil clearance between the coated molybdenum wall and the flow divider and to give a wall thickness of 40 mils for the flow divider. A high temperature was attained at a relatively low fuel input; however, the burner back pressure was still very high. A temperature of 1500°C was attained with a burner back pressure of 18 in. of water. No flash backs developed but excess air was needed to keep the flame from walking too far back into the heat exchanger.

The heater for diode No. 10 was also an innovation over previous diode heaters. The flow divider described for diode No. 9 was cut off to end 1/2 in. from the bottom. In this burner the combustion chamber was the bottom 1/2 in. of the thimble and no post-type combustion chamber made of silicon carbide was included. A temperature of 1550°C was observed with a pressure drop of 16 in. of water. Evidently the high pressure drop in premixed burners of this type is due to ignition of the gas-air mixture in the close clearance between the diode thimble and the flow divider. Ignition of the mixture abruptly increases the temperature, which decreases the gas density and increases gas velocity. The energy required to accelerate this gas must be supplied by an increased burner back pressure. This high burner back pressure is evidently inherent in a design employing premixed fuel and air to heat a thimble for a thermionic converter. It is one of the strong arguments for employing fuel injection for heating a thermionic diode internally.

Phase 2 - Fuel Injection Burner Development

There are several real reasons for starting out at this time on the development of a burner using the principle of fuel injection. The first is that higher burner efficiencies can be obtained than are practical in premixed burners. That is, a higher air preheat temperature can be attained without worrying about the problems of pre-ignition. In addition, the ultimate future use of gasoline, which has a lower ignition temperature, makes advisable the development of a fuel injection burner adaptable for use with several fuels. Finally, our experience with premixed burners has shown that it is possible to obtain the required high temperatures with premixed propane air burners but that the burner inevitably has a high pressure drop which evidently is not shared by even the unrefined types of fuel injection burners.

The first type of fuel injection burner tested is shown in Figure 2. Fuel is injected directly into the combustion chamber through a fuel injector made from stainless steel tubing, 0.070 in. OD and 0.052 in. ID. The end of the tube has been welded shut and four holes have been drilled in the side of the tubing, 90° apart and 0.010 in. in diameter. The pressure of the fuel flowing through these small holes causes the fuel to jet out towards the sides of the combustion chamber. It is important that the jets be positioned under the arms in the plug located inside the flow divider as shown in Figure 2. These arms of the plug prevent the exiting flue gases from blowing the flame up the exit tube before it has had a chance to come in contact with the bottom of the emitter thimble. The fuel then mixes with the preheated primary air coming down the outer annulus and moves into a toroidal-shaped eddy in the combustion chamber. When combustion is substantially complete, the flue gas enters the four exit ports around the plug in the exit tube and, on its way out to the exit, preheats the incoming air. A small amount of secondary air flows down around the fuel injector into the combustion chamber. Although this air is also preheated by the exiting flue gases, the main function of the secondary air is to cool the fuel injector to keep the injector from oxidizing and to keep the fuel from coking inside the injector.

The burner just described was used in Run VB-9. In this run the depth of the combustion chamber was 1/2 in. The burner functioned properly with a relatively high heating efficiency, high heat flux (considering the temperature of the emitter) and a low burner back pressure as shown in Table I. The

experiment was terminated after 3-1/2 hr running time due to failure of the Sn-Al coated molybdenum thimble.

The same burner hardware was employed in Run VB-10. A molybdenum thimble coated internally with TI-Kote was used as the emitter thimble. The depth of the combustion chamber was reduced to 3/8 in. It was decided at the outset to try for a continuous test of whatever duration was possible. During the first few hours, adjustments of air and fuel flows were made to give a temperature between 1300-1400°C with as little fuel expenditure as possible. For 42 hrs, hourly readings were taken and results of these readings are plotted in Figure 3. There seemed to be some random fluctuation in burning efficiency which lead to a wandering in the temperature between 1300-1400°C. Nevertheless, there appeared to be no deterioration in the performance of the burner. After 42 hrs the TI-Kote failed abruptly and the test was terminated. On examination of the burner after test, we found that the hot end of the fuel injector was oxidized but was still in operating condition, and that the tube conducting the secondary air to the combustion chamber was devitrified but still serviceable. The tube was made of quartz glass and devitrification was therefore expected. For a permanent burner, the tube could be made from coated molybdenum or TI-Kote material.

Other long-term tests are being conducted and will be reported in the next quarterly report.

TASK C - MATERIALS DEVELOPMENT AND EVALUATION

Phase 1 - Procurement and Evaluation of Emitter Thimble Materials and Coatings

Many of the flame heated thermionic converters built to date have failed due to loss of the anti-oxidation coating. Consequently, a new evaluation is being made of all possible sources of supply of coatings for molybdenum and also other refractory metals. Table II summarizes the coated material that has been obtained for evaluation on this project. An inexpensive screening test has been used which uses coated refractory metal wires 1/16 in. in diameter by 6 in. long. The wire was heated to incandescence by passing an electric current through it. An apparatus for doing this is shown in Figure 18 of the Second Quarterly Report[2]. An improvement has since been incorporated in some of the newer test stations. These stations use a coilless relay to sense
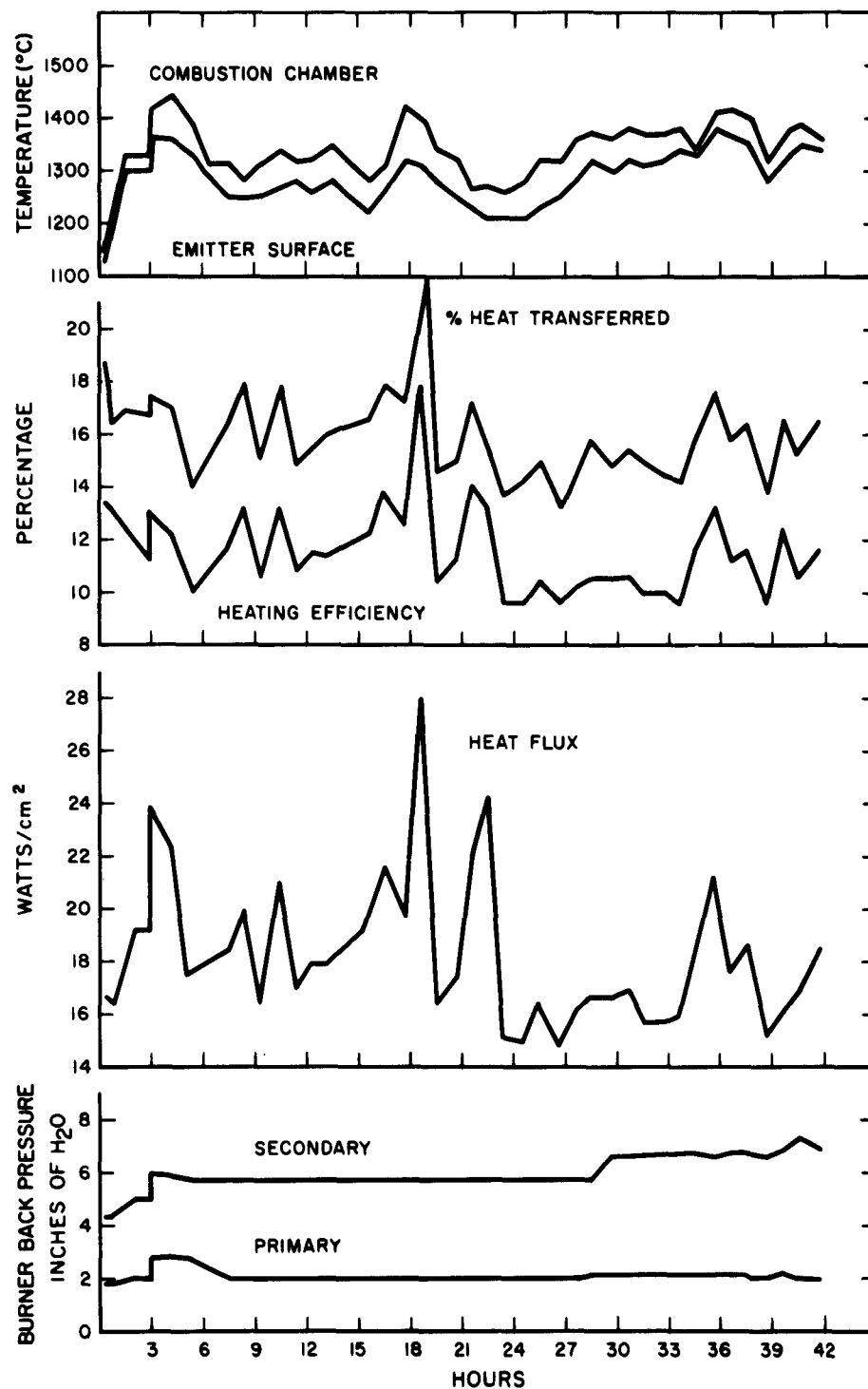
Figure 3. Result of Run VB-10

TABLE II

COATED REFRACTORY METAL SAMPLES
OBTAINED FOR EVALUATION

Source	No. of Wires	No. of Thimbles
Chromizing Corp., Hawthorne, Calif		
Durak-B on Mo.	123	36
KS coating to Ta	9	0
General Telephone & Elec Lab.		
Bayside, New York		
Al-Sn coating on Mo.	12	3
Thermomet Corp., Los Angeles, Calif.		
T-61 coating on Mo.	20	1
Texas Instruments		
Materials & Sensors Div.		
Dallas, Texas		
T1-Kote on Mo.	12	3
Raytheon Co., Waltham, Mass.		
Pyrolytic SiC on Mo.	24	0

the passage of the electric current through the wire. The relay is connected so that the electricity to the timer is interrupted when the wire burns out. At present, four test stations are in constant operation and six more are being constructed.

It must be emphasized, however, that the wire screening tests have merely been assumed to be equivalent to the real test which is the heating of a thimble internally with a flame. Enough results are now available on the testing of coated refractory metal thimbles to permit comparison of the performance of the thimbles with the performance of the wires ostensibly coated with the same material. The available results on each type of coating tested are presented in paragraphs a through d.

a. Durak-B Coated Molybdenum

Considerable work on the testing of wires has been reported in the first four quarterly reports.[2, 3, 4, 5] Coating thickness has been varied from 1.5 to 4 mils. Temperature has been varied from 1300 to 1750°C (brightness).

Wires have been tested in air (both stagnate and moving), in carbon monoxide, and in flames (both oxidizing and reducing). All these tests show that Durak-B gives good protection for fairly long periods of time. It has been observed that silica, the primary protective layer, devitrifies and becomes porous at approximately 1400°C and eventually leads to failure. If the wire is heated hotter than about 1400°C, the failure will occur in the transition zone between the hot portion and the cold portion of the wire near the clamp. A summary of all the previous wire data is given in Figure 13 of the Fourth Quarterly Report.[5] Some additional wire testing data on Durak-B was performed this quarter. As shown in Table III, these wire tests were performed at 1350°C in stagnate air

TABLE III

WIRE TESTING RESULTS - DURAK-B ON MOLYBDENUM

Wire Temperature: 1350°C
Atmosphere: room air
Coating Thickness: 0.004 in.

Wire No.	Time to Failure
B139266	549
B139271	590
B139272	402
B139273	441
B139274	376
B139280	560+ (shut down without failure)
B139283	629

on a wire with a 0.004 in. thick coating. Average time-to-failure for the seven wires was 507 hr with a low of 376 and a high of 629. Failure occurred somewhere in the devitrified portion of the coating. Figure 4 shows how a molybdenum wire coated with 0.004 in. of Durak-B looked after 376 hr in air. Wire temperature was 1350°C. Thus, a consistently good life is experienced for the thicker Durak-B coatings at a temperature near the expected operating temperature.

Some metallographic testing was done on a Durak-B sample, said to have a 0.0025 in. thick coating, which had been heated to 1350°C for 439 hr (see Table IV). Figure 5 shows a cross section of this coating before heating.

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Figure 4.   Durak-B Coated Molybdenum Wire
at Failure After 376 Hours at 1350°C

(Normal Light)　　　(Polarized Light)

Figure 5.　Durak-B on Molybdenum Before Heating (Magnification 500X)

TABLE IV

MISCELLANEOUS WIRE TESTING RESULTS

Wire Temperature: 1350° C

Atmosphere: Room air

Wire No.	Coating	Time to Failure (Hours)
B185324	Regular T-61	120
B185325	Regular T-61	116
B185326	Regular T-61	90
B185342	TI-Kote	5
B139247	2-1/2 mil Durak-B	439
B185304	Raytheon SiC (1st batch)	15
B185343	Raytheon SiC (2nd batch)	0.1

The thickness of the coating is 2.2 mils and the coating appears to have a band of voids in it and to have a columnar structure which shows up in polarized light. Figure 6 shows the same coating at the failure point. The coating now has expanded to a thickness of 4 mils and is divided into three zones. The outer zone is full of holes and deep cracks. The middle zone appears to be impervious and the inner zone appears to be an expanded reaction zone between the molybdenum disilicide and the molybdenum. Notice also that the cavity developing in the molybdenum undermines the coating.

All flame heated diodes constructed so far have been protected with Durak-B. The performance of the coating on these ten diodes is summarized in Table V. Notice that for the ten diodes the longest operating time recorded was 6 hr. In three out of the ten diodes failure occurred for other reasons than coating failure. A complete test of these diode coatings was therefore not accomplished. In addition to the diode tests, two Durak-B protected thimbles have been tested on the vacuum insulated burner experiment. The first was tested to a maximum of 1290°C for a total of 41 hr with no failure. Testing was suspended on this thimble because the observed heating efficiency was so very low. The second thimble lasted for 7.5 hr before a hole developed 0.1 in. from the bottom.

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Figure 6 - Durak-B on Molybdenum at Failure Point
(Magnification 500X)

The vendors of Durak-B think that the poor performance of the diode coatings as compared with a good performance of the same coating on the wire, may be due to error in the preparation of the thimble coating. The Durak-B coating is applied to both the inside and the outside of the thimble by a pack method. The inside of the thimble was then coated with two coats of Microstop lacquer and then the thimble was immersed in hydrofluoric acid to remove the molybdenum disilicide from the outside of the thimble. It is now believed that the Microstop lacquer may have had some thin spots in it which would allow the hydrofluoric acid to attack very small areas on the inside of the molybdenum thimble. The spots would then be sensitized to failure and would actually fail in a short time without having the coatings surrounding the failure point show any visible corrosion. This mode of failure was especially apparent in diodes No. 9 and 10. Accordingly, the thimbles to be used in future tests have been recoated both inside and out and then welded into a diaphragm assembly. No attempt has been made to strip the coating off the outside of the thimble.

TABLE V

FLAME CORROSION RESISTANCE OF DURAK-B COATED
MOLYBDENUM CUPS

Identity	Maximum Temp. (°C)	Time Till Failure. (hr)	Location of Failure	Comments
Diode 1	1300	3 hr	2 in. from bottom	see Fig. 10 of Ref. 4
2	1415	2-1/2+	no failure	
3	1415	5.7+ 3 cycles	no failure	
4	1550	1 hr	no failure	burner test
5	1410	4 hr	1/4 in. from bottom	under SiC cup
6	1560	1 hr +	not known	sample product
7	1600	2 hr	under SiC cup	
8	1650	6 hr	under SiC cup	
9	1500	2 hr	1 in. from bottom	
10	1535	1 hr	0. 3 in. from bottom	
*	1290	41 hr	no failure	massive SiC protection
†	1180	7-1/2 hr	0.1 in. from bottom	no SiC protection in combustion chamber

* Thimble used in burner tests VB-1 to VB-4

† Thimble used in burner tests VB-6 to VB-8

Figure 7 is a photomicrograph of a hole that developed in the
Durak-B thimble used in diode No. 9. Before it was mounted, the coating, shown
at the top of the photograph, extended across the hole almost entirely. However,
since this coating is very fragile the mounting process broke it away. Neverthe-
less, it is still evident from this photograph that the failure was due to a hemis-
pherical cavity growing out from a fault in the Durak-B coating. When the cavity
succeeded in eating through almost the entire thickness of the thimble, a leak
suddenly developed.
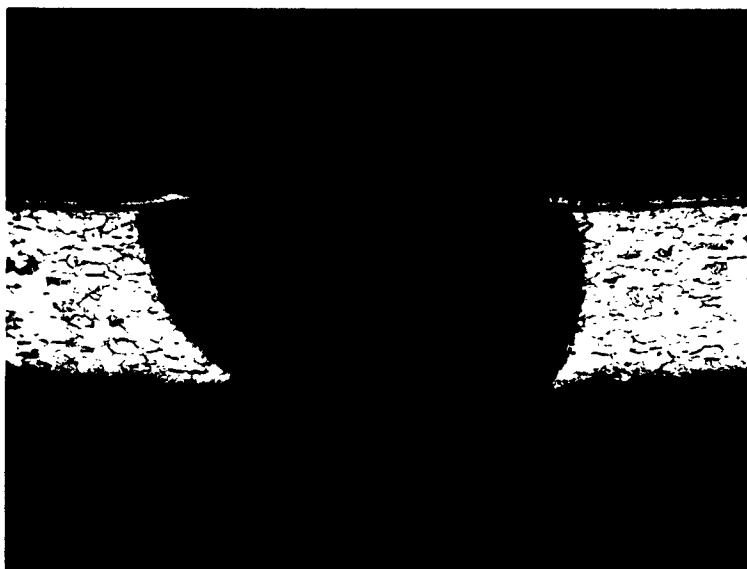
4-17-63   2414-4708
Figure 7.   Section Through a Hole Developed in the
Durak-B Coated Thimble Used in Diode 9.
(Magnification 75X)

b. Molybdenum Disilicide Coating (AI Process)

Interest was rekindled in the AI process for coating molybdenum
with an oxidation resistant coating due to one test which ran at 1350°C in air
for 710 hr. The results of all the wires from the batch of coated wires from
which this spectacular result was taken are shown in Table VI. Notice that the
other nine wires are consistently an order of magnitude below the 710 hr. The
reason why wire 35 should last so much longer than all the others is not known
at the present time; however, a difference is detectable by detailed examination
of this wire and some other wires in the batch. Some of this metallographic
examination on wire No. 35 is presented in this report.

AI-8124
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TABLE VI

WIRE TESTING RESULTS - AI CODE 247

Wire Temperature: 1350°C

Atmosphere: Room air

Wire No.	Time to Failure (Hours)
B139331	78
B139332	68
B139333	78
B139334	69
B139335	710
B139336	69
B139337	80
B139338	57
B139339	53
B139340	68

Figure 8 shows cross sections of coatings on three different portions of the wire in the transition region between the heated section and the section heated to 1350°C. Figure 8a shows a completely homogeneous coating having a thickness of 3.3 mils. Figure 8b shows the same coating in the cold part of the transition zone where the molybdenum has not yet recrystallized. Notice that the coating is essentially the same thickness, but that a thin intermediate layer has begun to develop. In Figure 8c the molybdenum has recrystallized and the thickness of the coating has increased enormously. The inner layer is apparently about 2 mils thick. Figure 8c is especially interesting because a fissure appears to have developed in the outer layer. A cavity appears to be just developing at the top of this intermediate layer. In Figure 9a the same area is photographed under lower magnification. The top coating has a thickness of 5.4 mils and is half inner layer and half outer layer. There seems to be one or two instances of a fissure developing in the outer layer and a cavity starting in the inner layer. At the bottom coating, a large cavity has developed in the molybdenum metal. This cavity appears to have developed from a fissure in the outer coating which caused the inner coating and the molybdenum to be eaten away. Also, the inner coating appears to be decreased in size near the
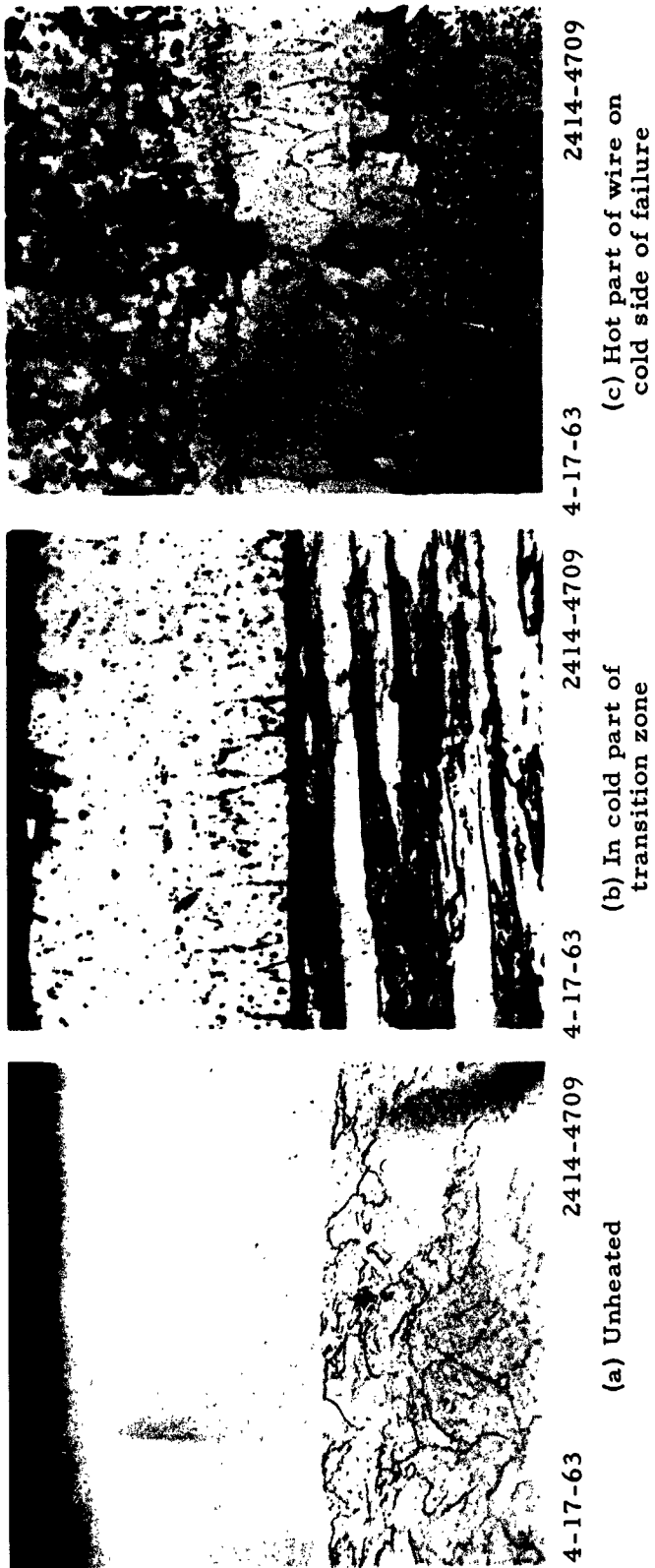
Figure 8. Cross Sections of a Molybdenum Wire Coated with Modified MoSi$_2$ by AI Process (Code 247). (Magnification 500X)
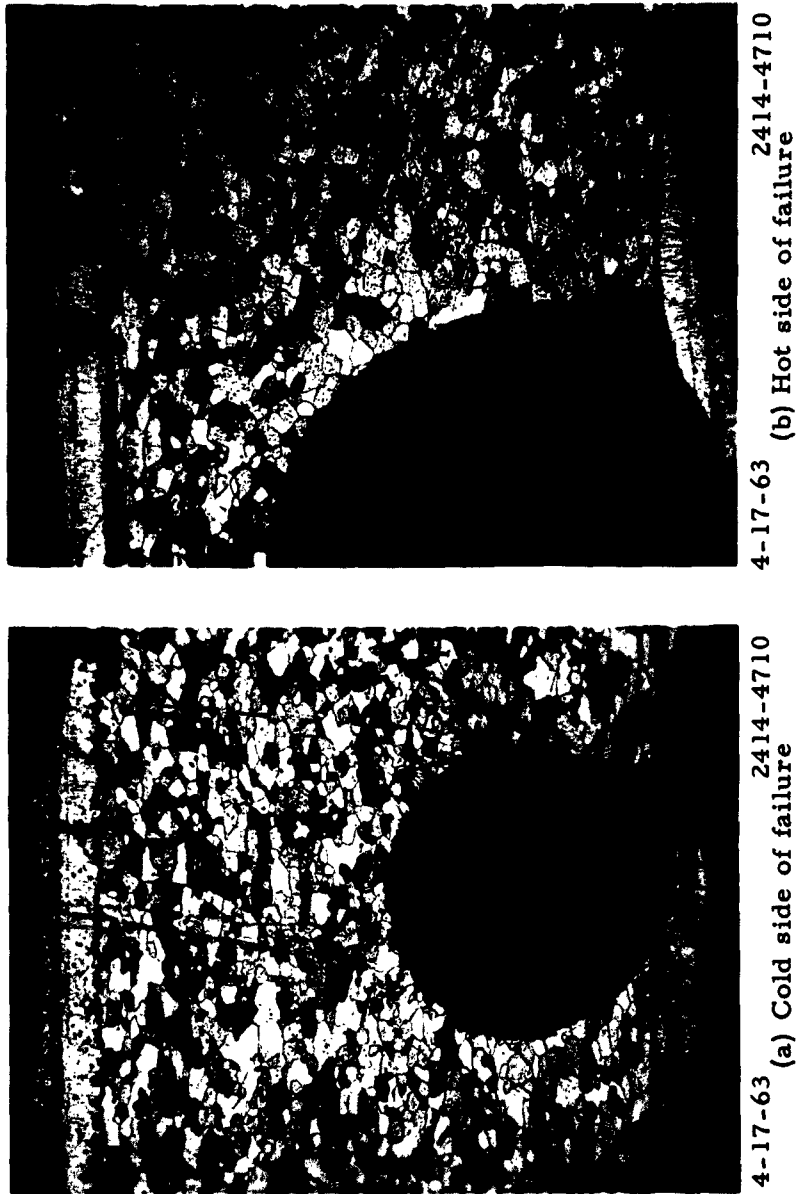
(a) Unheated

(b) In cold part of transition zone

(c) Hot part of wire on cold side of failure

4-17-63   2414-4710   (a) Cold side of failure

4-17-63   2414-4710   (b) Hot side of failure

Figure 9.   Cross Sections of Molybdenum Wire Coated with Modified
MoSi$_2$ by Al Process (Code 247).   (Magnification 75X).

cavity. Figure 9b shows part of the large cavity which caused failure and the coatings on the hot side of this failure. Notice that the inner layer is very large here.

This phenomena of buildup at the inner layer of a molybdenum disilicide coating with time and temperature has been noted by R. L. McKisson previously and is summarized in Figure 34 of the Third Quarterly Report.[4] This buildup of intermediate layers in the molydisilicide coating is shown graphically in Figure 10 which is a composite photomicrograph of the transition zone in a wire test of Durak-B. The cross section shown here is not through the diameter of the wire. Toward the left the section is mostly through the coatings.

In the hot portion of the wire between the two failure points, the coating appears to be of a somewhat different character as shown in Figure 11. It is about 3 mils thick and the inner transition layer is relatively unimportant. This inner layer almost disappears in the region of the small cavities which have developed at almost regular intervals along the wire. One of these small cavities is shown at a higher magnification in Figure 12. Obviously this coating can be improved even further if the self-healing properties of the coating could be prolonged to keep fissures from developing into the interior.

c. Aluminum-Tin Coating on Molybdenum

The aluminum-tin coating has been developed by the General Telephone & Electronics Laboratory specifically for tantalum, although it has been found to work well on tungsten and molybdenum. Some of the early work and development of this coating has been reported by D. D. Lawthers and L. Sama of the General Telephone & Electronics Laboratory, Bayside, New York.[6] Twelve molybdenum wires were submitted to the Laboratory for coating with a suitable tin-aluminum protective layer. Ten of these wires were tested in the standard wire testing rig with the results shown in Table VII. The time-to-failure for these wires falls over a much wider range than the two molybdenum disilicide coatings just described. Time-to-failure varies from 10 hr to 196 hr with a fairly even spread in between. Two wires were subjected to a thermal cycling test from room temperature to 1350°C. This test was used previously on some Durak-B coated molybdenum wires which lasted for over 3120 cycles without failure (see Table IV of Reference 5). The failures of the aluminum-tin coatings after 500 cycles or less therefore shows that this coating is sensitive
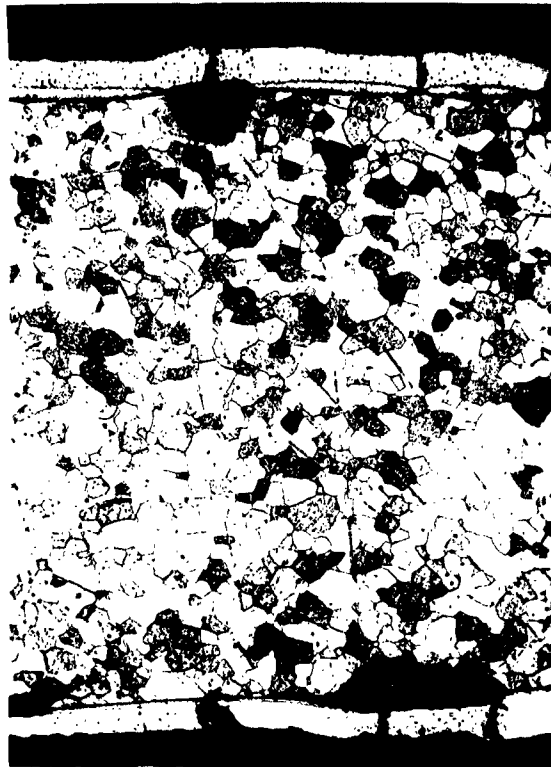
ESTIMATED EXPOSURE TEMPERATURE
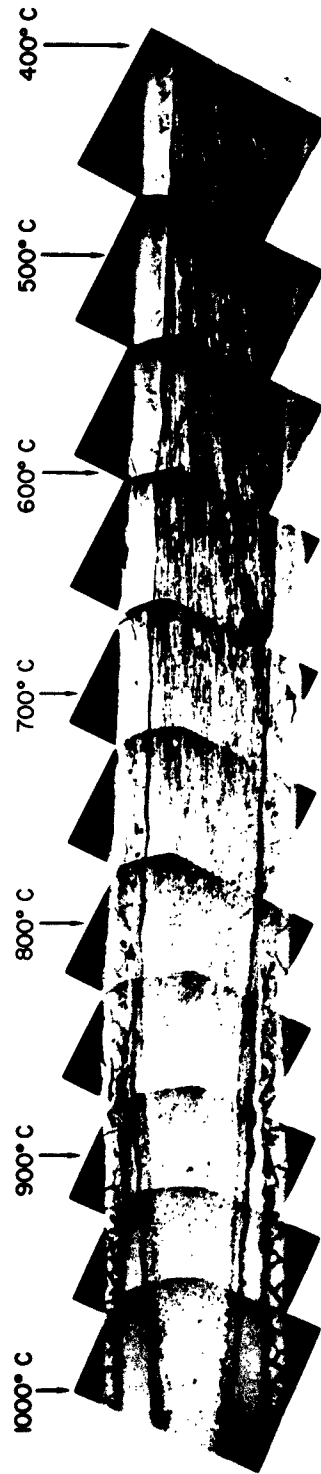
Figure 10. Cross Section of a Durak-B Coated Molybdenum Wire
Showing the Buildup of Intermediate Layers

4-17-63   2414-4711

Figure 11.   Cross Section of Molybdenum Wire Coated with MoSi$_2$
(Modified) by AI Process (Code 247) (Magnification 75X)

4-17-63   2414-4712

Figure 12.   Cavity in Hot Section of AI Coated
Molybdenum Wire (Magnification 500X)

AI-8124

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TABLE VII

WIRE TESTING RESULTS - Sn-Al ON MOLYBDENUM

Wire Temperature: 1350°C
Atmosphere: Room air
Coating Thickness: 0.003 in.

Wire No.	Time to Failure (Hours)
B185330	53
B185331	133
B185332	10
B185333	96 (one power interruption)
B185334	196
B185336	94
B185337	178
B185338	16
B185339	64
B185341	63
	Thermal Cycling (Cycles)
B185335	501
B185340	234

to thermal cycling. Figure 13 shows a typical tin-aluminum coated molybdenum wire after failure has occurred. Notice that the coating has a metallic luster near the clamp where the wire never got very hot and then the coating takes on a dull appearance over most of the length of the wire. Near the break, however, a crystalline growth appears, which appears to be made up of pinkish or purplish needles. K. T. Miller of Atomics International has analyzed these needles using X-ray diffraction and the results appear in Table VIII. In addition to the pinkish crystals, the following were also detected: a pinkish-white sponge made from tin oxide; a green sponge made from molybdenum and molybdenum oxide; and black flakes made from tin oxide, molybdenum oxide, and aluminum oxide. It is interesting to note that tin oxide (SnO_2) decomposes and melts at 1127°C, which is considerably lower than the test temperature and especially the temperature of the section undergoing failure immediately before failure occurs.

4-17-63   2414-4728

Figure 13.   Tin-Aluminum Coated Molybdenum Wire Test at Failure

TABLE VIII

PRODUCTS OF CORROSION OF Sn-Al COATED MOLYBDENUM WIRE

Sample	Major Phase	Minor Phase	Other
Pink Crystals	SnO_2	--	--
Pink-White Sponge	SnO_2	--	--
Green Sponge	MoO_2	Mo	--
Black Flakes	SnO_2	MoO_2	Al_2O_3 Mo_9O_{26}

Some examples of the tin-aluminum coating have been examined metallographically. Figure 14 shows the tin-aluminum coating as it appears under ordinary light and under polarized light. The coating is 3 mils thick. The phase identification is a tentative one based on analogy with tantalum and by comparing these photomicrographs with similar ones found in Reference 6. According to the vendor the coating is applied as a spray paint made up of tin powder, aluminum powder and a nitrocellulos binder. When the paint is dry it is vacuum heat treated at 1040°C to cause the aluminum to react with the refractory metal substrate. Figure 15 shows this coating after it has been heated in air for a period of time. Figure 15a shows the coating after 10 hr exposure at 1350°C. Its maximum thickness is now 4 mils. The phases in the coating are difficult to interpret but it appears that the light phases are aluminum rich and the dark phases are tin rich. Figure 15b is a section of the coating after it has survived 196 hr at 1350°C. This coating is approximately 9 mils thick on the average and the continuous coating near the molybdenum has essentially disappeared. The small black areas in the body of the coating are presumably the tin rich phase, and the dark areas near the molybdenum substrate are voids. Evidently the tin has almost evaporated.

Three deep-drawn molybdenum thimbles were coated on the inside with a tin-aluminum. One of these thimbles was tested in burner test VB-9. It was heated up twice without failure but failed immediately after being heated the third time. Total time at temperature was 3-1/2 hr and maximum temperature was 1130°C. Failure was brought about by two holes in the side of the thimble. One hole was 0.68 in. from the bottom and the other 0.76 in. from the bottom. Since the thimble heater in this case was a fuel injection type, the flame could not

4-17-63   a) Ordinary Light   2414-4713
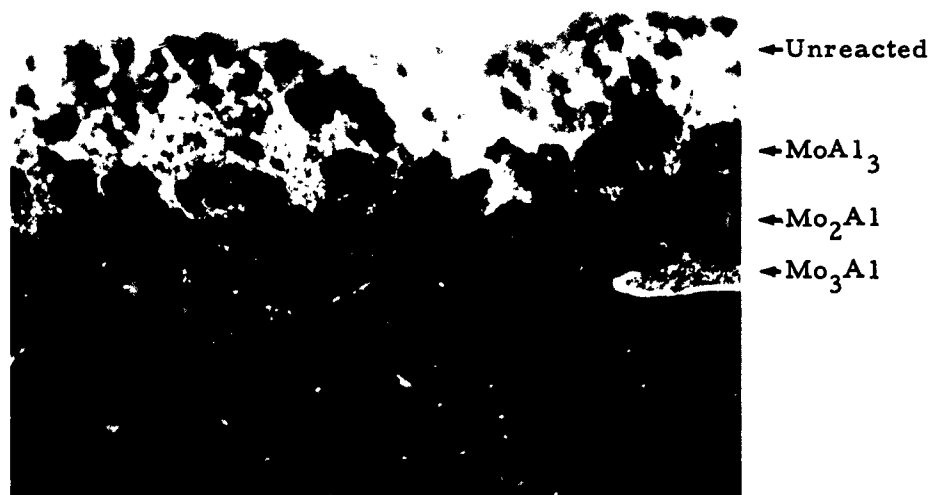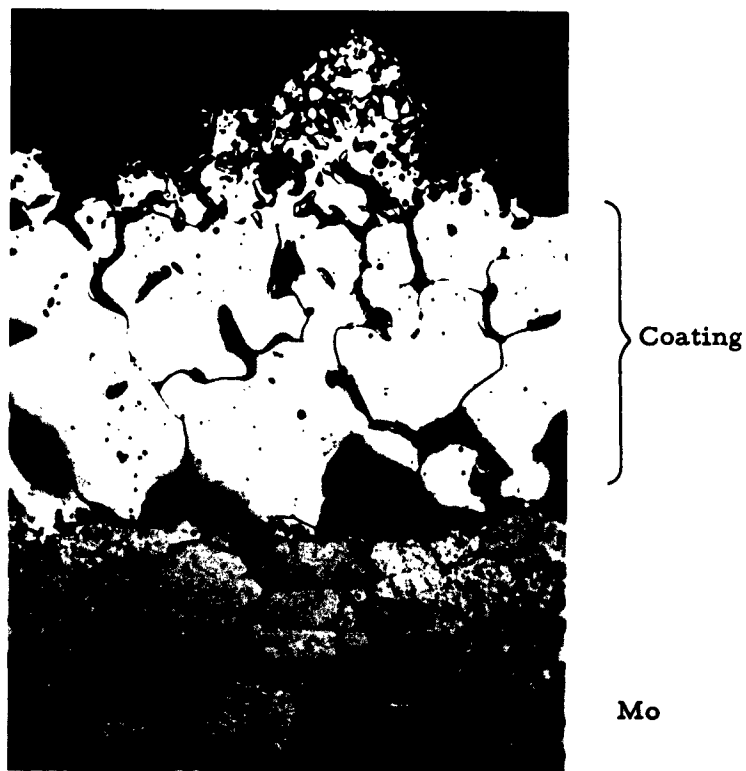

4-17-63   24-414713
                       b) Polarized Light

Figure 14. Tin-Aluminum Coating Before Heating
                 (Magnification 500X)

Mounting

Coating

Mo

4-17-63   2414-4714
(a) 10 hrs. at 1350°C (Magnification 500X)

Coating

Mo

4-17-63   2414-4714
(b) 196 hrs. at 1350°C (Magnification 250X)

Figure 15.   Tin-Aluminum Coating After Heating

possibly get up above 1/2 in. from the bottom. Consequently, the coating failure occurred in the high temperature end of the air preheater. Figure 16 shows a cross section of a hole which was eaten through the molybdenum cup used in VB-9. The coating is 3.3 mils thick at the point of failure and the molybdenum is 13.3 mils thick. It is again obvious that the hole developed from a cavity developing underneath the coating, and that the coating bridged over the cap cavity almost completely, at least up to the point of failure. Besides the two failures, the rest of the coating on the inside of the molybdenum capsule was gray and rough, similar in appearance to the coatings on the wire tests. However, no pink crystalline masses were visible.
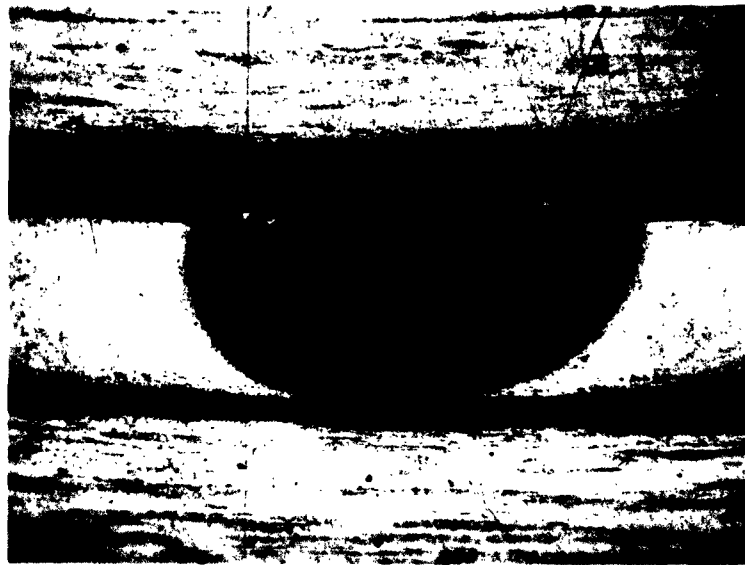
4-17-63   2414-4715

Figure 16 - Hole Eaten Through a Molybdenum Thimble
Coated on Inside with Tin-Aluminum (Magnification 75X)

d. Pyrolytic Silicon Carbide Coating

Some testing was done during this quarter on two types of pyrolytic silicon carbide. One type of pyrolytic silicon carbide applied by Raytheon was tested with two separate batches applied to the outside of a 1/16 in. diameter molybdenum wire. Most of the wires received were only partially coated. Only one wire appeared to be completely coated with an irregular coat up to 0.040 in.

thick. This wire was tested at 1350°C in air and lasted 15 hr. The results are shown in Table IV.

The other type of pyrolytic silicon carbide tested was TI-Kote, applied by Texas Instruments, Materials and Sensors Division. An attempt also was made to apply this coating to the outside of a 1/16 in. diameter molybdenum wire. On cooling the wire down from the temperature of application, the coating flaked off on all but one of the 12 wires. This one wire was tested and lasted for 5 hr before failure. The failure was brought about by the development of microscopic cracks in the coating which allowed a small amount of air to diffuse into the molybdenum; then the characteristic hemispherical cavities developed until one of the cavities occupied the entire wire diameter and then failure occurred.

The application of TI-Kote to the inside of a deep drawn molyb-denum thimble was also attempted. In this case, one of the three thimbles tried had a complete coat. In the other two cases, on cooling down, the coating spald off of the bottom of the thimble. A picture of these three coatings, showing especially the bottom of the thimbles, is shown in Figure 17. The third thimble was used in run VB-10 and was subjected to temperatures of 1300-1400°C for 42 hr before failure. Figure 18 shows the outside bottom of this thimble after failure occurred. Notice that for the first time failure occurred through the bottom of the thimble instead of through the sides. The big hole shown in this figure developed in less than 4 min of operation after the leak developed. Sub-sequent to this test the apparatus was modified so that the vacuum pump and the fuel flow would stop when vacuum was lost.

The bottom portion of the capsule was sawed off to inspect, at closer range, the cavities which had developed from the inside. Figure 19 shows how the inside of the bottom of the capsule appeared. The cavity which resulted in failure is near the edge at 4 o'clock, and there is another cavity al-most as deep near the edge at 2 o'clock. Finally, there is a cavity just begin-ning to develop about half way out at 11 o'clock. Around this last mentioned cavity is a stain which appears to indicate that the coating had come loose from the molybdenum right around the cavity. The light colored area in the picture is where the TI-Kote spald off on cooling down. This coating did not come loose at high temperature; if it had, a much more severe attack on the molybdenum would have taken place.

Figure 17. Inside View of Molybdenum Thimbles Coated Internally with TI-Kote

4-17-63

2414-4716

4-17-63   2414-4717

Figure 18. Outside Bottom of TI-Kote Coated Molybdenum Thimble
After 42 Hours at from 1300 to 1400°C

2414-4718

Figure 19.   Inside Bottom of a TI-Kote Coated Molybdenum Thimble
After 42 Hours at 1300 to 1400°C

This coating is unique in that the weakest part of the protective film is the flat bottom of the capsule and not the rounded sides. It appears that this coating is very impervious and quite strong in compression, but it is not noted for its tenacious bond to the molybdenum substrate. In fact, when this thimble was sawed apart, the portions of the coating which had not been heated came loose from the molybdenum as if there were no bond between them at all. The reason why the coating system works at all probably lies in the differential thermal expansion of the two materials. Molybdenum has a thermal expansion coefficient of 5.5×10^{-6} per $^\circ$C. TI-Kote has an expansion coefficient of $4.0\text{-}4.9 \times 10^{-6}$ per $^\circ$C. Thus when TI-Kote is applied to the inside of a molybdenum thimble at high temperature and then cooled down, the molybdenum shrinks more than the TI-Kote and the TI-Kote is definitely in compression. Across the flat bottom of the thimble this compressive force in the TI-Kote caused some of the coating to relieve itself by pulling away from the molybdenum and breaking off. On the sides, because of the curvature, this mode of failure was not possible and very good protection was achieved. The obvious solution then is to use a bottom with some curvature all the way across so that the weakness shown up in this batch will not be evident.

Phase 2 - Gas Permeation Measurements

a. Theory

Permeation of gas through metals or ceramics takes place in three stages:

(1) Absorption of the gas on the surface of the solid

(2) Diffusion through the solid

(3) Desorption from the outer surface of the solid

Theoretically, any of these three steps could be controlling but in actual practice the diffusion step is usually controlling.

The rate of diffusion of a gas through a metal is specific for the metal and the gas. That is, the diffusion rate is not affected by the presence or absence of grain boundaries or is not a function of the size of the gas molecule. For instance, hydrogen, nitrogen and carbon dioxide diffuse through iron at high temperature while helium does not. Finally, diffusion of diatomic gases

like hydrogen through metals takes place in the atomic state. Thus, the diffusion rate is proportional to the square root of the gas pressure.

Ceramic materials behave quite differently from metals. In ceramics like glass, helium diffuses more readily than hydrogen. Hydrogen diffuses through the more open lattice of glass as a hydrogen molecule and therefore the rate of diffusion is proportional to the first power of the hydrogen pressure.

The relationship expressing the amount of diatomic gas diffusing through a solid metallic barrier is customarily given by the following equation.

$$Q = \frac{DAt}{d} \left[\sqrt{P_1} - \sqrt{P_2} \right] \exp \left(-\frac{E}{RT} \right) \tag{1}$$

where Q = amount of gas permeating the barrier (std. cm^3)

D = permeation constant (cm^2/hr)

A = area of barrier (cm^2)

d = thickness of barrier (cm)

t = time (hr)

P_1, P_2 = pressure on inlet and outlet of barrier, respectively (Atmospheres)

E = activation energy for process (cal/gm mole)

R = gas constant (cal/gm mole)

T = absolute temperature (°K)

For permeation through a ceramic body equation (1) is used with the square root signs removed. A composite barrier would, of course, complicate analysis. In addition, the concentration of hydrogen in the flame that heats a thermionic diode is not known with any accuracy because appreciable hydrogen concentration is a transient effect. There appears to be appreciable hydrogen present because it explains the high heat transfer rates that are experienced in flame-heated thermionic diodes. Nevertheless, it is usually an intermediate product in combustion and goes through a maximum in the luminous zone of the flame.[9]

These considerations have lead the authors to the conclusion that gas permeation through flame-heated thermionic converters must be measured directly. At least the permeation through the emitter assembly, when heated with the burner, should be measured. Other experiments could be devised which would give good scientific data comparable with and extending the work found in

the literature but the application of these data to the prediction of gas permeation in a specific diode would be impossible.

b. Comparison with the Literature

Before presenting additional data obtained during this quarter on the permeation of hydrogen through coated molybdenum, it would be instructive to compare the data already obtained and reported in the last two quarterly reports[5,1] with data for other materials which have been reported in the literature. Figure 20 shows such a comparison. In previous reports the permeation rate in micronliters/hr/cm^2 of surface area had been plotted versus the reciprocal of the absolute temperature. This is an Arrhenius plot which should allow the data to fall on a straight line if the data follow equation (1). In Figure 20 the permeability plotted on the ordinate is different from that given in previous quarterly reports in that it includes the thickness of the barrier being permeated in the denominator. The plot in Figure 20, however, does not include any effective hydrogen pressure since in some cases the actual hydrogen pressure is not known. The abscissa of Figure 20 used a linear scale for temperature instead of the reciprocal scale of the absolute temperature because this allows easier interpolation of the data. Data which would fall on a straight line in an Arrhenius plot are slightly curved in Figure 20. The most surprising thing in Figure 20 is that the data obtained at Atomics International for permeation of hydrogen from a flame through Durak-B coated molybdenum is only about an order of magnitude less than permeation of pure hydrogen through pure molybdenum. That is, at 1000°C the hydrogen permeation through pure molybdenum is .25 cc (STP)/hr cm^2 mm with 1 atmosphere H$_2$ pressure difference and the permeability through Durak-B coated molybdenum from a flame atmosphere to a vacuum is 0.03 cc(STP)/hr cm^2 mm. One interpretation is that the Durak-B coating has essentially no effect on the permeability of molybdenum and that the effective concentration of hydrogen in the flame is 1%. It is difficult to see how the concentration of hydrogen in a flame would be this high. Molybdenum is noted for its low permeability to hydrogen. Copper, which is also used in some thermionic diodes, has almost as low a permeability but pure nickle is greater by an order of magnitude. The permeabilities of other metals of interest are shown in Table IX. Notice that the permeability varies over a wide range and is very selective as to the gas. Since the Durak-B coating obtains its resistance to oxidation by having a thin layer of silica on the outside, it is interesting to
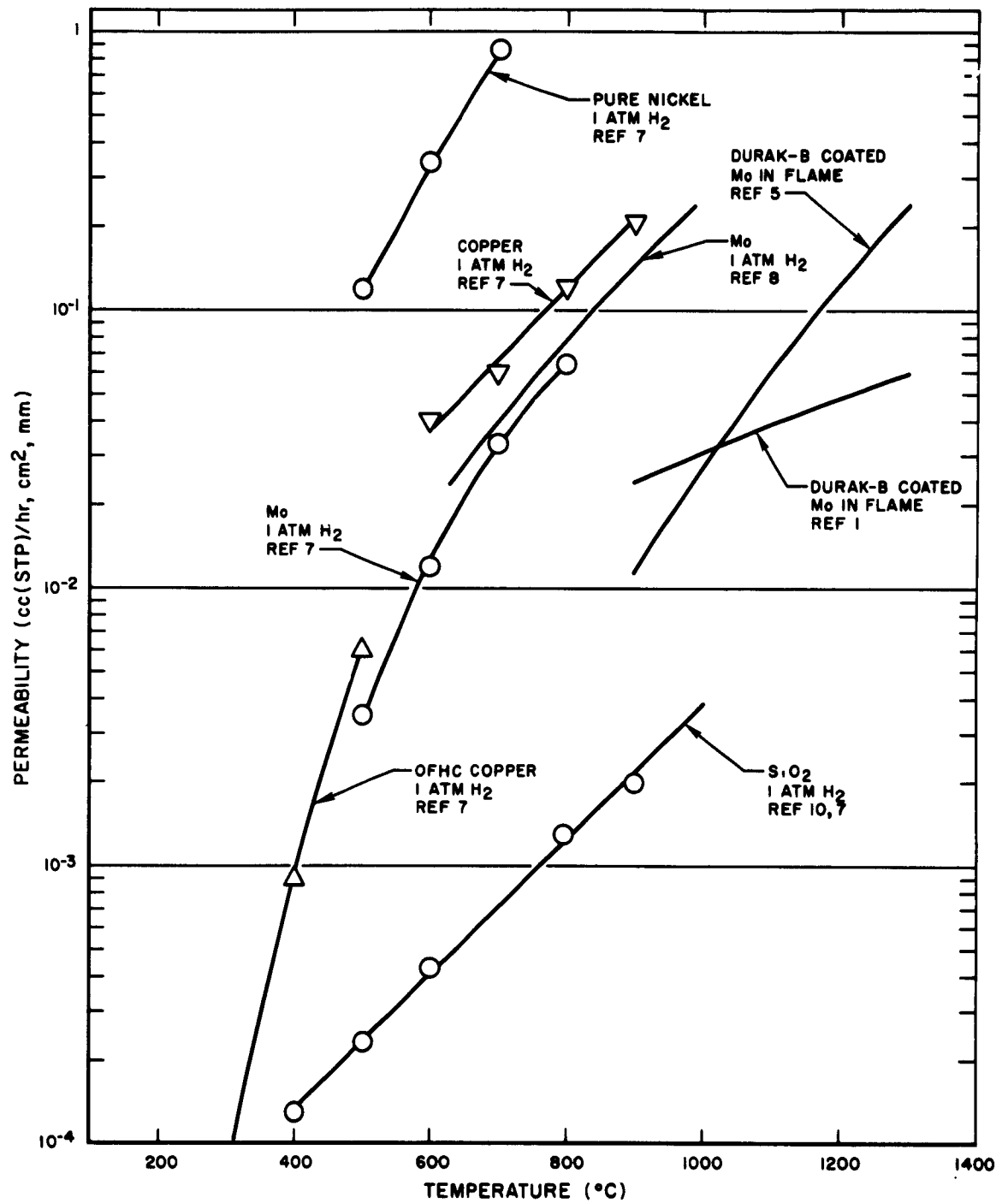
Figure 20. Permeability of Hydrogen

TABLE IX

### PERMEABILITIES OF METALS TO GASES AT 1000°C

Metal	Gas	Permeability cm^3 (STP)/cm^2 hr mm (1 atm gas pressure)	Ref.
Pd	H_2	745	11
Nb	H_2	300	8
Ni	H_2	5.0	11
Pt	H_2	0.7	11
Cu	H_2	0.06	11
Cu	H_2	0.4	7
Mo	H_2	0.3	11
Mo	N_2	0.0002	11

compare the permeability of silica with that of Durak-B coated molybdenum. Even though Figure 20 shows that silica has a permeability an order of magnitude lower than Durak-B and two orders of magnitude lower than molybdenum, the thickness of the layer developed and the effective hydrogen pressure difference is of importance in determining the effect it will have when used in a composite coating.

Although up to the present the permeation of hydrogen through the emitter thimble of the thermionic converter has been the greatest concern, it is also possible that some hydrogen may permeate through the collector thimble. Consequently, the data shown in Figure 21 are of some importance. Here the permeability of different stainless steels are compared. Notice that the permeability to one atmosphere of hydrogen for 303, 304, 347 and 410 stainless steels are very close to each other. A coating of Solaramic enamel applied to 303 stainless steel has been shown to reduce its permeability by a factor of 10. It is very interesting to note, however, that stainless steel in the vicinity of 600 to 800°C exposed to air with a normal content of water will usually pass an appreciable quantity of hydrogen. Most of the hydrogen comes from the decomposition of water on the surface although some hydrogen is contained even in dry air. Thus, 410 stainless steel and 304 stainless steel exposed to normal room air have from 1 to 5% of the permeation experienced with these materials when they are exposed to pure hydrogen. Note that all stainless steels have
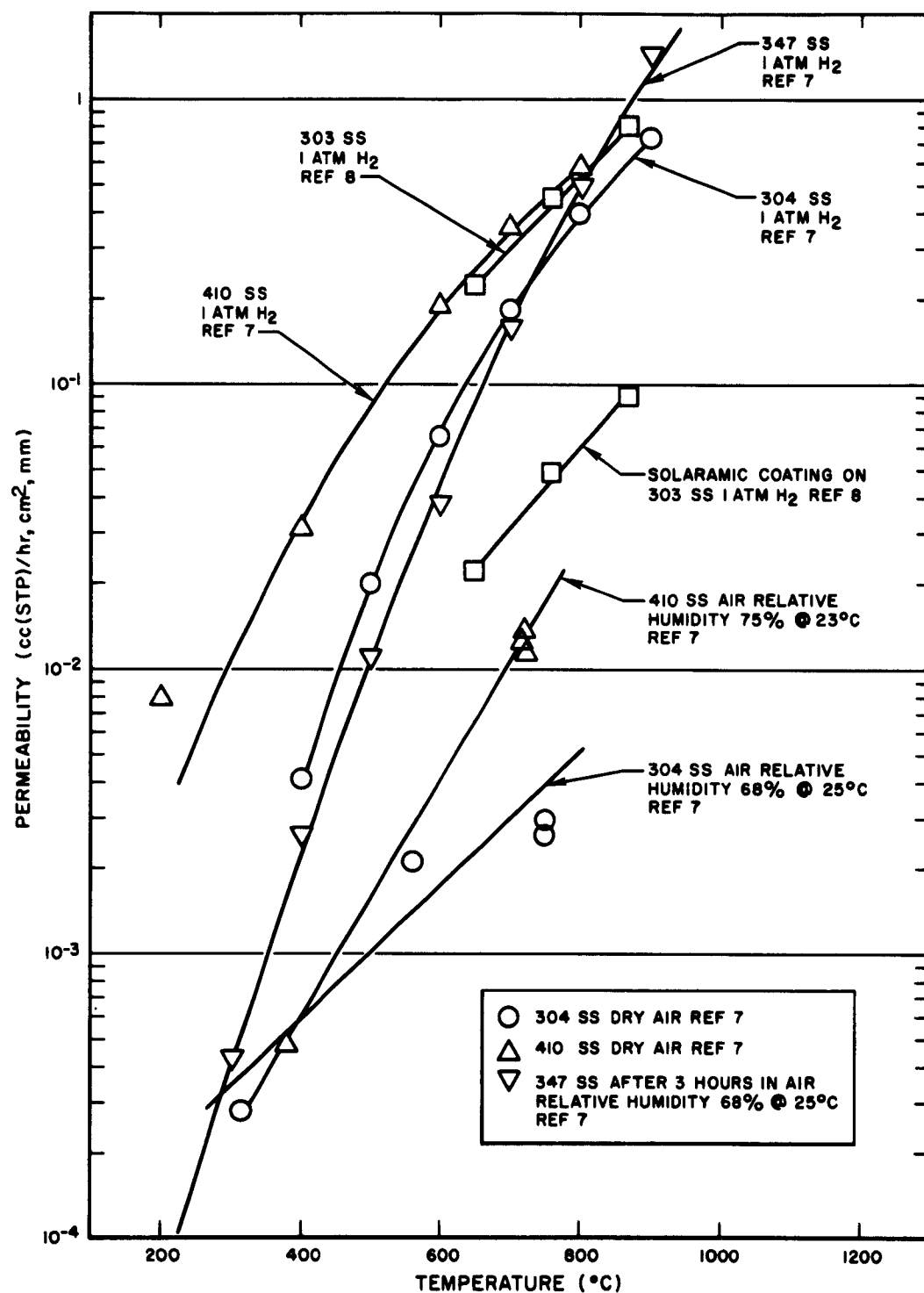
Figure 21. Permeability of Hydrogen Through Stainless Steel

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about 0.1% of the permeation rate shown for pure hydrogen when exposed to dry air. It should be emphasized that the permeating gas is still hydrogen even with dry air. The most important part of the data shown in Figure 21 is the fact that 347 stainless steel, after being aged for 3 hr or more in room air, develops an oxide film which renders the stainless steel very impermeable to hydrogen from a moist atmospheric air source. Thus the collector thimble of the thermionic converter should be made from 347 stainless steel. The thimbles which have been used have been made from 304 stainless steel. These data also raise the question as to what the permeability of Kovar, used in some parts of the diode, is to atmospheric air. Kovar is about as resistant to atmospheric corrosion as mild steel and therefore water vapor will decompose on surface to from metal oxide and hydrogen in the metal. Thus, an effective high permeability would be exhibited. Figure 20 shows that silica has a low permeability to hydrogen as compared with metals. Compared with glasses, however, silica has one of the highest permeabilities. There seems to be as much of a spread in the permeabilities of glasses to hydrogen as there is in metals.[7]

c. New Data

During this quarter additional measurements of the permeability of Durak-B coated molybdenum were made using the apparatus shown in Figure 15 of the Fourth Quarterly Report.[5] As in the past, the temperature of the flame has been measured with a chromel-alumel thermocouple and the permeation rate has been determined by a pressure rise method using a McLeod gage. In addition, there has been an attempt during this series of measurements to observe the air-gas ratio used in the Brewer furnace which furnishes the flame atmosphere for the capsule. The results for this third series of measurements are given in Table X. These results are plotted in Figure 22 and are compared with results reported in the last two quarterly reports. These new results generally fall upon a line parallel to the lower line from previous measurements, but somewhat lower. There is some indication from the measurement of air-gas ratios that the flame atmosphere is somewhat more important than the flame temperature. More careful measurements must be made, however, to determine this for certain. For instance, Runs 10, 11 and 12 were taken at a lower air-gas ratio than most of the others.

Equation (1) shows that when the hydrogen pressure in the flame is equal to the hydrogen pressure inside the capsule, permeation through the
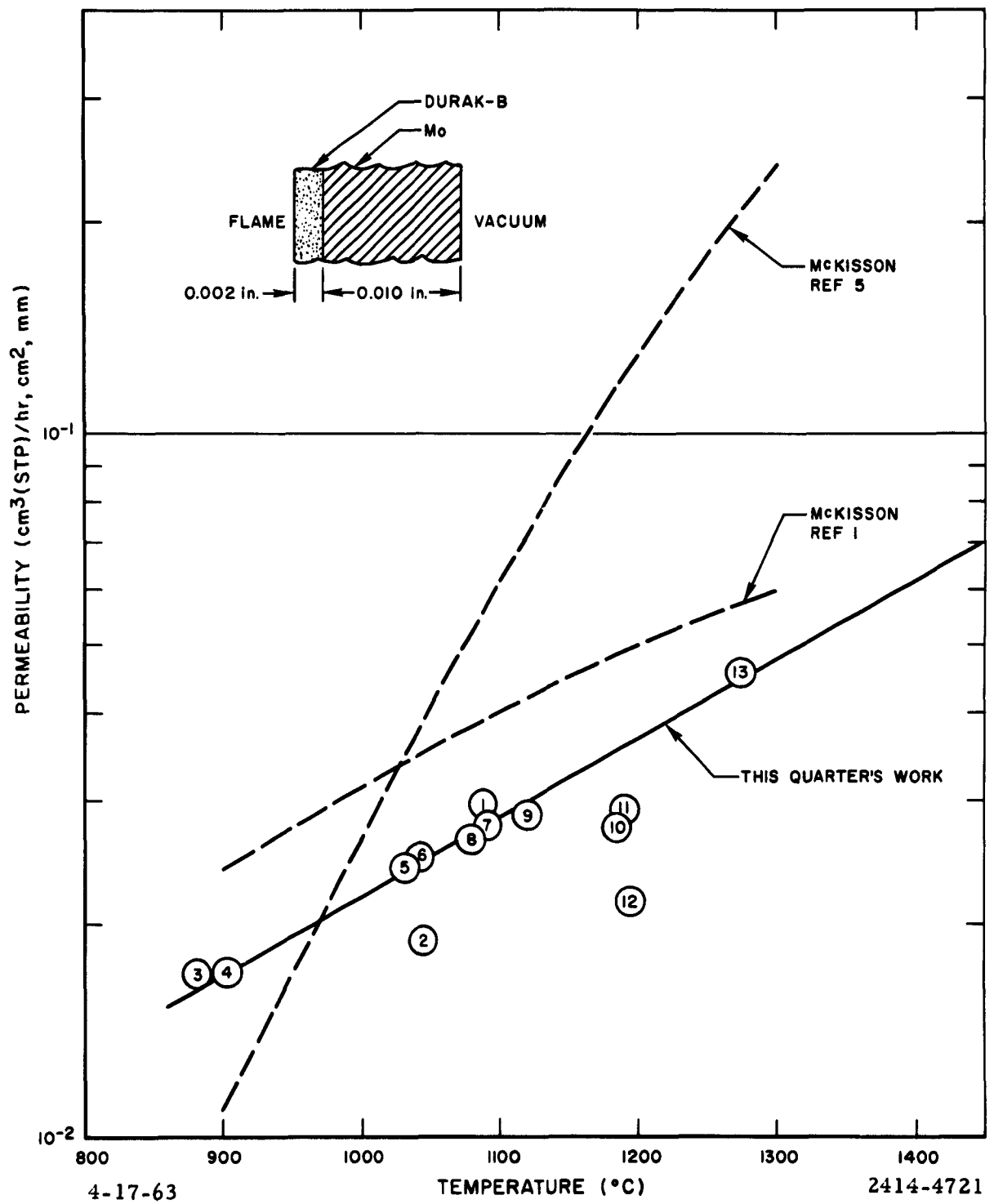
Figure 22. Permeability of Durak-B Coated Molybdenum

TABLE X

GAS PERMEATION MEASUREMENTS FOR DURAK-B COATED
MOLYBDENUM IN A FLAME

(Third Series)

Run No.	Temperature	Permeability cm^3 (STP)/hr cm^2/mm	Air–Gas Ratio
1	1086	2.93×10^{-2}	2.45
2	1045	1.89×10^{-2}	2.45
3	882	1.70×10^{-2}	1.3
4	903	1.70×10^{-2}	-
5	1032	2.40×10^{-2}	2.25
6	1042	2.49×10^{-2}	2.25
7	1090	2.38×10^{-2}	2.35
8	1080	2.58×10^{-2}	2.35
9	1120	2.86×10^{-2}	1.5
10	1185	2.74×10^{-2}	1.5
11	1190	2.9×10^{-2}	1.5
12	1195	2.14×10^{-2}	1.5
13	1273	4.59×10^{-2}	-

capsule should stop. That is, it is theoretically possible to determine the effective hydrogen pressure in the flame by determining the equilibrium hydrogen pressure inside a capsule immersed in the flame where the capsule itself will only pass hydrogen. In Figure 23 the gas permeation data are reproduced in which we followed the pressure rise curve up to the limit of the measurement on the McLeod gage, 300 microns. This measurement required over an hour in some cases and the temperature of the furnace remained substantially constant during this period as shown in Figure 23. Evidently much longer times, and capacity to measure much higher pressures must be employed before a measurement of the effective hydrogen pressure in the flame is possible. If a reaction is taking place on the capsule surface in which water vapor is decomposed and hydrogen is liberated to the metal, then a leveling off of the pressure rise curve should not occur.
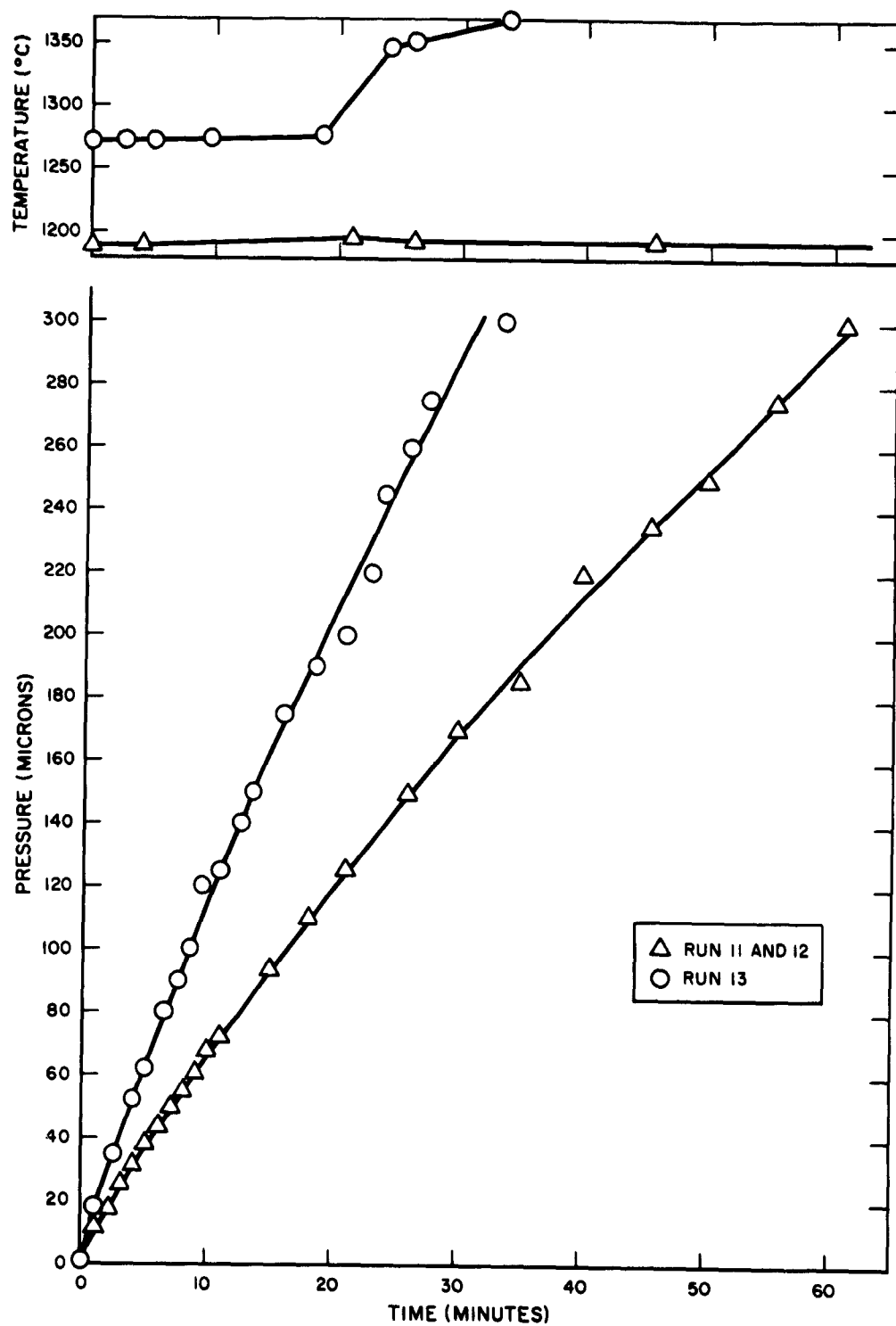
Figure 23. Gas Permeation Data

TASK D - PROTOTYPE DEVELOPMENT

Phase 1 - Testing Flame-Heated Converters

Converters No. 9 and 10 were tested during this report period. These tests are described under Task B, Phase 1. Neither converter ran long enough to produce any electrical output data.

It has been decided that emitter assemblies will be heated instead of completed diodes until an emitter assembly with a reasonably long life at temperature is obtained. Some of these emitter assemblies will be tested with the emitter surface cooled by a heat sink at the rate of 20-40 w/cm^2. Some will be tested with heaters designed for high heating efficiency. In order to illustrate what direction the development is taking, Figure 24 has been prepared to show how the next flame-heated diode test might look. Of course, some of the features shown in this drawing have not been tested at the present time and may turn out to be different. Figure 24 shows that the primary air enters and passes over the lower portion of the pins of a pin-fin heat exchanger and then passes down through the outside triangles of the primary heat exchanger to the combustion chamber. The preheated air mixes with the fuel in the combustion chamber and burning takes place. Some air is brought down around the fuel injector to keep the injector cool. The flue gas from the combustion chamber then passes up through the inside triangles of the primary heat exchanger and through the top part of the secondary heat exchanger to the outside. Notice that this experiment employs three jack screws to vary spacing between the emitter surface and the collector surface. Generally accepted heat transfer correlations have been used to make heat transfer calculations for this configuration. The results, however, tend to be too optimistic and they will be presented after experimental verification is available.

Phase 4 - System Design and Construction

The goal of this phase is to develop and construct a thermionic power source sample product having at least two separately fired diodes. In principle, each diode and associated heating equipment will be similar to that shown in Figure 24. However, instead of using a variable spaced converter, a fixed space converter will be constructed using the information gathered in testing variable spaced converters. We intend to design the converters so that they will be screwed in like light bulbs (see Figure 25). The electrical connections to the

SECTION AA'

PIN FINS

PRIMARY HEAT EXCHANGER
FUEL INJECTOR
UPFLOW
FOAM PLUG
DOWNFLOW

SECTION BB'

FUEL (PRO
SECONDA

A

C

C

CLAMP

B

SEALOFF

SECTI

FUEL (PROPANE OR GASOLINE)

SECONDARY AIR

PLUG FOR LIGHTING HOLE

PIN FINS

FLUE GAS

SECONDARY HEAT EXCHANGER (PIN-FIN)

A   A

C

PRIMARY AIR

JACK SCREWS (3 REQD)

CLAMP

DIAPHRAM

Ti-Zr GETTER

CESIUM RESERVOIR

SEAL AND INSULATOR

RADIATION SHIELDS

FOAM PLUG

B   B

A

COMBUSTION CHAMBER

EMITTER (6.1 cm²)

COLLECTOR

6 INCHES

DOWNFLOW

SECTION BB'

SEALOFF

SECTION CC'

2414-4723

Figure 24. High Thermal Efficiency
Flame-Heated Thermionic
Converter Experiment

AI-8124
49

EXHAUST

INLET MANIFOLD

AIR

FUEL INLET

INSULATING STRUCTURAL MATERIAL

TEMPERATURE CONTROLLER JUMPER

SCREW IN DIODE

COLLECTOR
EMITTER
COMBUSTION CHAMBER
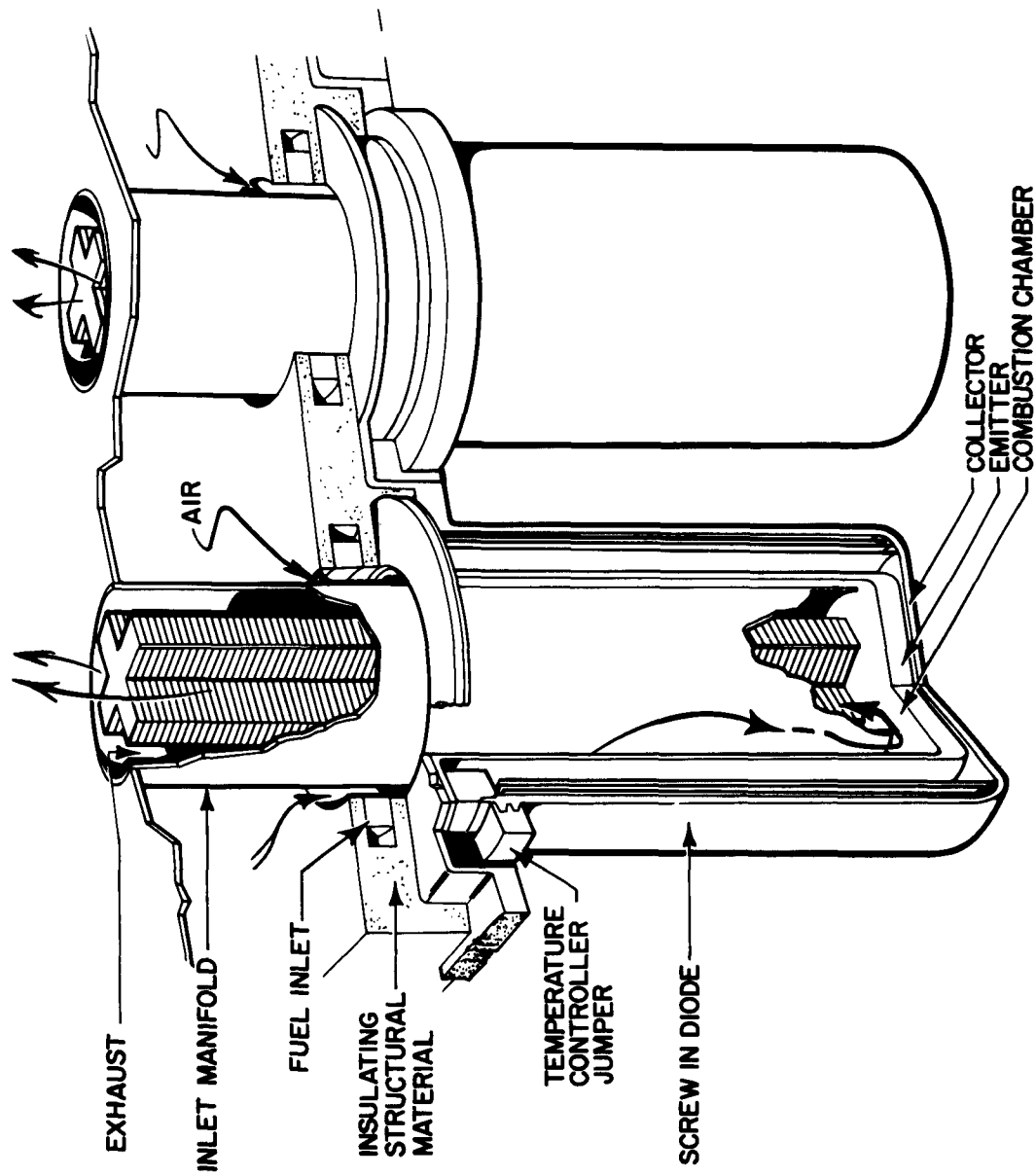
2414-4724

4-17-63

Figure 25. Internally Fired Thermionic Converter

converters will be temperature controlled so that the part of the diode in contact with the connections will act as cesium reservoirs. It should be noted that Figure 25 shows a design employing a premixed burner for the converter heater. A fuel injection burner similar to that shown in Figure 24 or Figure 2 is preferred. No matter what type of burner is used, however, the design shown in Figure 25 permits construction of a light weight and compact power source since no furnace insulation is required and most of the heat exchanger is inside the converter. Such a design would have a big advantage in attaining a high power-to-weight ratio and in attaining power in a short period of time, since no unnecessary mass must be heated to operating temperature. Since burning is a volume phenomena, the smaller the scale of the combustion chamber the larger becomes the problem of attaining complete combustion. Results to date (see Task B) indicate that a satisfactory combustion chamber can be developed.

The converter concept shown in Figure 25 was used to construct a model of a proposed power source employing 6 converters connected in series. Figure 26 is a photograph of this model fully assembled. Figure 27 shows this model partially disassembled, revealing the 6 converters and how they can be removed for replacement.

2414-4725

Figure 26. Model of a Thermionic Power Source
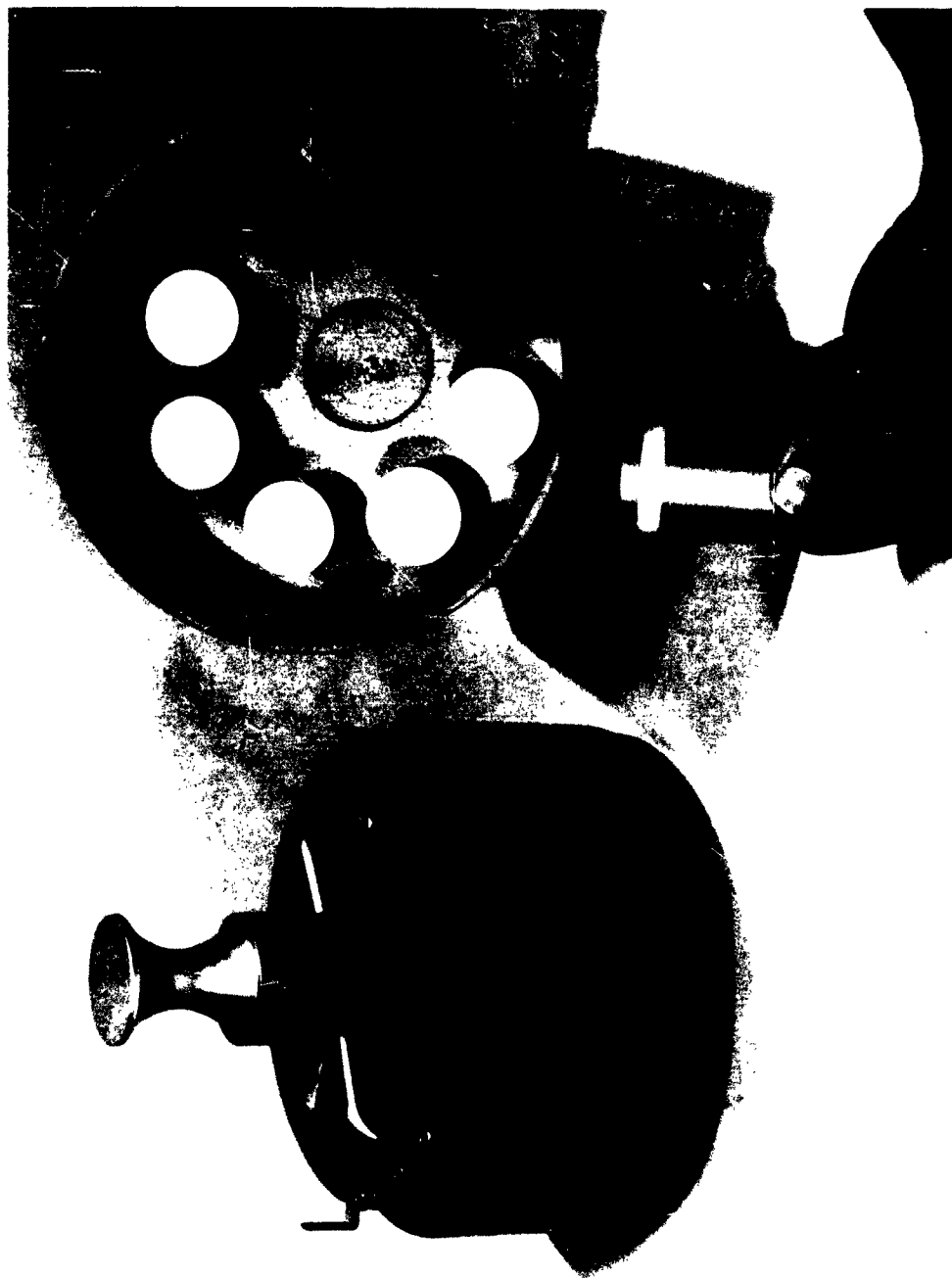
Figure 27. Model of a Thermionic Power Source Partially Disassembled

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CONCLUSIONS

1. Fuel injection burners applied to the internal heating of an emitter assembly, 1 in. in diameter by 3 in. long, have been built and can be perfected.

2. TI-Kote applied to the inside of a molybdenum thimble is a promising anti-oxidation coating provided the flat bottom of the thimble can be rounded sufficiently.

PROGRAM FOR NEXT QUARTER

TASK A - DIODE DEVELOPMENT

Design and procurement of parts for a fixed-space, flame-heated thermionic converter will begin.

TASK B - HEAT SOURCE DEVELOPMENT

The vacuum-insulated heating experiment will be used in development of higher efficiency fuel injection burner designs. Higher efficiencies will be obtained by employing better mixing of fuel and air and by using an efficient external heat exchanger.

TASK C - MATERIALS DEVELOPMENT

Hot shell testing will continue.

KEY PERSONNEL ASSIGNED TO PROJECT

		Hours Worked During 6th Quarter
D. H. Adair	Senior Mechanic	295
E. V. Clark	Research Engineer	111
R. G. Cole	Mechanic-Eng. Lab., Junior	137
H. Hori	Research Engineer	194
W. R. Martini	Project Engineer	414
J. D. Nogy	Senior Mechanic	440
A. J. Riccio	Advanced Technical Personnel	126

ADDITIONAL BIOGRAPHY

H. Hori - Research Engineer, Thermionics Group, Thermionics and Thermo-electric Department, Research Division

Education

College	Year	Degree
West Coast University	1949-1952	B.S., Mechanical Engineering

Experience

Place	Year	Field
Atomics International	1959-present	Thermionic diode design, construction, and test. Developed variable spacing diode. Design of guard ring variable spacing diode.
	1958-1959	Mechanical properties testing on thorium and titanium alloys. Testing on ceramics sapphire, beryllium oxide, and varied ceramic mixtures.
	1954-1957	Research on cold work effects and radiological damage effects on copper and copper alloys.
	1952-1954	Physical properties test on pure metals and alloys.

Publications

"Internal Friction and Shear Modulus of Thorium at High Temperatures," Co-author with C. E. Dixon, American Society of Mechanical Engineers Nuclear Engineering and Science Conference, March 11-14, 1957

"Processes for Liquefying Small Amounts of Hydrogen," Co-author with R. Dahleen, NAA-SR-MEMO-1078, August 1954

"The Vapor Pressures and Densities of Liquid Fluorine-Oxygen Mixtures,"
   Co-author with D. D. Cubiciotti, NAA-SR-MEMO-1173, November 1954
"Measurement of Young's Modulus," Co-author with C. E. Dixon,
   NAA-SR-MEMO-1222, January 1955
"Progress Report on Physical and Mechanical Properties on Titanium Alloys,"
   NAA-SR-MEMO-423, July 1955
"Second Annual Technical Summary Report for Basic Research in Thermionic
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AD

Atomics International, Canoga Park, Calif.
FLAME HEATED THERMIONIC CONVERTER RESEARCH
by W. R. Martini, D. H. Adair
6th Quarterly Report, 1 Oct. - 31 Dec. 1962
27 pp illus.
(Report No. AI-8124)
(Contract DA 36-039 SC-88982)

Unclassified Report

New types of welding techniques have been developed for attaching the coated molybdenum thimble to the converter assembly.

Although satisfactory temperatures and heat fluxes were obtained with burners using premixed air and gas, the development of burners using fuel injection directly into the combustion chamber was started. Satisfactory burners employing fuel injection have now been obtained.

A number of anti-oxidation coatings for molybdenum are now undergoing evaluation, both in the form of coated wires heated electrically and in the form of thimbles heated internally with a flame. One thimble coated internally with TI-Kote was heated for 42 hours at a maximum temperature of 1400°C before failure occurred.

(over)

1) Combustion Chambers
2) Combustion Chamber Liners
3) Molybdenum Compounds and Silicides
4) Silicon Compounds and Carbides
5) Inverter Rectifiers
6) Diodes (Electronic Tube Devices) - Cesium Vapor
7) Power Supplies (Power Equipment)

I Thermionic Converter Research
II Martini, W. R.
III Adair, D. H.
IV U.S. Army Electronics Research & Development Laboratory, Ft. Monmouth, New Jersey
V Contract No. DA 36-039 SC-88982

AD

Two flame-heated converters were tested during this report period. Some power was developed but failure in the coating occurred before any data could be obtained. A model of a multi-diode power source using individually heated diodes is presented.

UNITERMS

Thermionics
Converters
Diodes
Molybdenum
Molybdenum Disilicide
Protective Coatings
Combustion
Durak-B
Propane
Gasoline
Silicon Carbide
TI-Kote

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